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Perspectives on Biochemical Electricity

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As an introduction to the first symposium on biochemical fuel cells, this paper briefly considers various aspects of a new but already diversified field.

In view of its novelty and the scarcity of publications, bioelectrochemistry has had more than its fair share of publicity. This and the fact that the biological aspects are not too well grasped by many science administrators have hindered its progress. However, a gradual change of attitude is becoming apparent.

Both empirical experimentation and fundamental approaches should be pursued for optimum rates of development in the art and science of biochemical fuel cells. Three distinct methods of operation are already under study: imitation of life processes for generating electricity, indirect use of biological reactions to generate products useful as fuels, and direct use of organisms or enzymes on electrodes to act as fuel-cell catalysts. While any one of these lines of study may lead to useful devices, each is bound to increase our knowledge of life processes and is thus likely to have some serendipic effects.

The usefulness of biocells to the civilian power economy of an industrial nation is likely to remain insignificant for a very long time. Conventional fuels, power generating stations, and motive engines are difficult to compete with as concerns costs, chemical reaction rates, and power densities. Specialty products that might find a civilian market are likely to be introduced *via* military or other Government needs. The Army, for example, may be able to use biochemical fuel cells for remote, inaccessible signaling devices or in guerilla warfare.

On the other hand, bioelectrochemical power could conceivably be of great significance to fuel-poor underdeveloped countries. Materials such as organic matter in fresh and salt water, plant and animal debris, garbage, and body wastes can all be considered as potential sources of electricity. Possible uses include communication, water purification, irrigation, lighting, heating, and cooling. Author

Introduction

THIS, as far as I am aware, is the first symposium anywhere devoted to the problem of converting biological to electrical energy by direct electrochemical means. The concept may be summarized as follows.

> The disintegration of organic compounds by micro-organisms is accompanied by liberation of electrical energy. . . . The electrical effects are an expression of the activity of the micro-organism and are influenced by temperature, concentration of the nutrient medium, and the number of active organisms present . . . [2]. The bacterial culture during the process of energy conversion is in a sense, therefore, a primary electrical half-cell, and as such should conceivably be able to perform work. [1]

These citations are taken from a paper by Potter, published in 1912, and one by Cohen given at Boston in 1930. Potter obtained 1.25 ma from six cells of yeast plus glucose versus pure glucose solution. Cohen built a bacterial battery "furnishing cur-

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rent of about 2 ma. at a pressure of 35 volts." This concept is relatively novel as compared with Grove's inorganic chemical fuel cell, which antedated it by some 70 years. Of course, Galvani's bioelectric discovery about 1780 started the science of electricity, and I shall have occasion to refer later to that kind of biocell.

Even after all these years, however, the definition of fuel cells is still being debated. It is doubtful whether a universally acceptable one can be established by decree or a committee. Let us tentatively define fuel cells as devices in which unlike chemicals are combined with each other electrochemically to produce electrical power. The chemicals are added on demand, and products are removed as required. Thus, the only difference between a conventional electric battery and a fuel cell is that the former is self-contained and has a limited output period before it is discarded or recharged. The fuel cell is not self-contained and, if properly put together, should operate virtually indefinitely, as long as two (or more) suitable unlike chemicals are supplied and the products drained off.

The preceding definition is broader than some others advanced thus far. Microorganisms in fuel cells, for example, might continue to generate fuel even when there is no demand for it, thus perhaps creating a toxic environment for themselves. Again, regenerative (inorganic) fuel cells have been built in which hydrogen and oxygen are combined to obtain power, or water is electrolyzed by using an outside power source. Thus, both processes take place in the same cell, and the gases may be stored there also. Is this a fuel cell, a gas storage battery, or both?

'Conventional' Fuel Cells

Conventional fuel cells will be reviewed first to gain a better perspective on the competitive position of biochemical fuel cells with respect to their closest relatives.

The simplest and most advanced types of fuel cells utilize hydrogen and oxygen. Current densities are on the order of 50 to 500 amps/ft^2 of electrode, and operating voltages are 0.5 to 0.9 volt per cell. Cells with ion-exchange membranes instead of liquid electrolyte cannot yet sustain such current densities, but they can often be made thinner. Thus, more of them can be packed into one cubic foot. Compared with internal combustion engines, all such fuel cells have a low power density (horsepower per pound). Unless there is a "breakthrough," they are unlikely to become acceptable power sources for ordinary passenger cars or for airplanes. However, they could be useful for relatively low-powered portable devices, to replace batteries in larger or special vehicles, and as stationary power sources.

The energy density of a fuel-cell system, i.e., the product of power and time divided by weight of fuel cell plus fuel plus accessories, can easily be greater than that of other power sources, particularly for extended missions. Thus, a hydrogen-oxygen fuel cell is slated for use in NASA's Apollo project. This primary, or once-through, system will have to carry an adequate fuel and oxidant supply on its mission and is estimated to weight about half a ton, which is 1/6 the equivalent weight of silver-zinc batteries, assuming 80 watt-hours/lb. for the latter. The potable reaction water, a useful by-product, would be of no earthly value.

Cells using air instead of oxygen will be more practical for most earth-bound applications, particularly after improvements have been made in the air cathode. Hydrogen may be carried in small devices, or generated chemically on the spot. Larger units might be coupled with a reformer or cracker to enable operation with conventional petroleum fuels, alcohols, or ammonia, but with some loss of efficiency. Direct ammonia fuel cells are another possibility, though performance still needs improvement.

Research is in progress to develop a low-temperature fuel cell operating directly on alcohol and air, with an acid electrolyte. The CO_2, formed by oxidation of the alcohol, would carbonate the usual alkaline electrolyte for hydrogen fuel cells and increase the electrical resistance or even precipitate potassium carbonate at the electrode.

The operating temperature must be raised to obtain satisfactory reaction rates if saturated hydrocarbons are to be used directly. No catalysts have yet been discovered that would do the job at reasonable densities and low temperatures. Little has been done with fuel cells operating directly on hydrocarbons at intermediate temperatures, i.e., 150° to 450°C. However, they might be useful for certain automotive and stationary uses.

Beyond this temperature range, molten alkali carbonates have been used as electrolytes in high-temperature fuel cells. The corrosive electrolyte is usually contained in a solid matrix of magnesia or mixed with magnesia to form a paste under the operating conditions. Such carbonate cells can be operated directly with methane plus steam as fuel, or the reactants can be reformed first in an adjacent space. This kind of fuel cell has been considered for home and plant use. Intermittent operation of cells operating much above ambient temperature requires either a warm-up period or intermittent external heating.

Oxides such as ZrO_2 have been employed as solid electrolytes at still higher temperatures, i.e., near 1000°C. It is too early to assess the usefulness of this kind of fuel cell, a potential competitor of the molten carbonate cell.

During the last few years, R&D expenditures have risen for these and other fuel cells, including the regenerative ones and those using more expensive, unusual fuels or oxidants. Program costs have been estimated at about $15 million per year spent by industry and some $5 million by the U. S. Government. These do not include the all-out hardware efforts on Apollo and Gemini by NASA. No commercial fuel cells are being sold, and indications are that industry is slackening its efforts again, apparently having found that commerical possibilities are currently rather limited. Special-purpose fuel cells for military and space use undoubtedly will become a reality, though no one system will fill all the requirements for every purpose to which fuel cells might be applied.

Therefore, except for governmental uses, the 'conventional,' or nonbiochemical, fuel cell does not look as imminently practical today as it did only two years ago. Not only do technical problems remain, such as low power-to-weight and power-to-volume ratios for short missions, but investment and operating costs are also still too high.

Where, then, do biochemical fuel cells stand?

Approaches

Proponents of biochemical fuel cells are not unanimous concerning the type of effort needed. One group proposes an empirical approach to create operative devices. Another desires a thorough, fundamental, long-range approach to understand completely the thermodynamics, mechanisms, and kinetics before attempting to build any devices. Therefore, it seems obvious that both approaches should be practiced simultaneously and in moderation.

A full understanding of bioelectrochemical processes is needed to optimize biochemical fuel cells. Such knowledge will take years, if not decades, to accumulate. Conversely, most of you have meanwhile seen or heard of a biochemical fuel cell that powered a small transmitter.

As a parallel example, I might mention that we now have an excess productive capacity for manufacturing ammonia, yet Ph.D. theses and original scientific papers about the chemistry of the process are still being published.

The two avenues of attack – fundamental and empirical research – are not mutually exclusive but complementary and should be carried on simultaneously.

Methods

As far as I can ascertain, efforts in this segment of science (or technology?) have branched into three different directions: 1) to imitate life processes; 2) to use such processes indirectly, for generating chemicals that can be used in fuel cells; 3) to use biological materials, primarily bacteria or their enzymes, as catalysts directly in fuel cells, usually deposited on electrodes.

The first method obviously demands the creation (or existence) of a good working model of whatever process is to be duplicated and hence a fairly profound understanding of natural events before we can hope to imitate them. Specifically, one project funded by the Air Force had as its objective "the simulation of the process through which certain species of biological life produce electrical power." The final report, "Study of Bioelectric Energy Sources," contains a literature review of bioelectricity and the results of a study of electric phenomena in knifefish and electric eels. It also reports on the preparation of very thin nonselective protein-lecithin membranes.

The easiest method appears to be that of using microbiological means for generating a fuel. Methane from sewage became commercial some years ago. Unfortunately, methane is useful only in high-temperature fuel cells, being virtually inert in low-temperature cells. On the other hand, hydrogen-producing bacteria are known which, if adaptable to suitable ambient conditions, could be coupled with 'conventional' hydrogen-air fuel cells. Perhaps someone [in this room] today can point the way to, or has already put together, a biochemically fuelled hydrogen-oxygen or hydrogen-air fuel cell.

The use of bacteria or enzymes as catalysts in fuel cells might be considered of intermediate difficulty between the other methods. Nevertheless, as we shall hear later, such systems are a reality today. The major novelty in this field is the attachment of enzymes or organisms to one or both electrodes. This procedure may change the future development of biochemical fuel cells profoundly. We shall hear more about it [from other speakers later in the program].

Just as ordinary catalysis is still largely an art, bioelectrocatalysis also seems to depend on the direction of the wind and the phase of the moon. These mysteries of today will be the recipes of tomorrow, given enough time and manpower for research.

Uses

Let us consider some of the reasons for the current interest in biochemical fuel cells. From a global point of view, such devices promise yet another source of energy for underdeveloped countries, especially those that do not own fossil fuels. Until the cost of electrical power from solar and nuclear energy is reduced substantially, and unless wind and water power (or perhaps geothermal sources) can make significant contributions to satisfy their growing energy demands, such fuel-poor countries might consider obtaining biochemical electricity from their sea and/or land resources.

Especially attractive would be methods for using waste or unclaimed materials, such as garbage, body wastes, or organic matter in fresh or salt water. Bioelectricity might be harnessed for agricultural uses, desalination of water, heating, and lighting. Even relatively primitive biocells might power radio receivers. Economical biocells could thus be of far-reaching importance to underdeveloped areas.

Such systems will require cheap and simple structures and controls. They must be relatively foolproof, too. For example, the danger of displacement of a useful microorganism by an intruder must be minimized. This may be possible by choosing an organism that operates near one or the other extreme of the pH scale. Perhaps the natural rate of growth of organisms can help control the output of the biocell. It remains to be seen whether the biocell will indeed be useful to underdeveloped countries.

The civilian economy of industrialized nations appears to stand to gain relatively little from biochemical electricity for the present. Fossil fuel, the work horse for the majority of stationary power plants, is still cheap and plentiful. Power densities of biochemical devices are minuscule thus far, so that biocells for motive power plants seem out of the question now. Whether they will ever be considered for such use is still debatable. Specialty products might find a market, however. Such products, if any, are likely to result from military or other government efforts in the field.

The military is interested in unconventional power sources for a variety of reasons. Since I am quite familiar with its needs, let me cite some of the Army's hopes for such sources. In tactical applications, power plants should be as unobtrusive and hard to detect as possible. Ideally, therefore, the Army wants silent power devices, with high efficiency and high power density – i.e., of small volume and light weight – that operate at ambient temperature and do not give off noticeable products such as noxious gases or steam. These devices should be simple, have few or no moving parts, have long life, require little maintenance, and be operable on a variety of fuels. Actually, some of these ideals are far from attainable, and some are incompatible with each other. For example, one must compromise between high efficiency and high power density, or between high power density and long life, or between low temperature and low cost of fuel.

As I see it, biochemical fuel cells are no panacea here, either. This may, however, have some qualities that will make them particularly applicable to special uses. For example, they could conceivably supply energy for signalling systems that must function for long periods without refueling or any other attention. The metabolic rates of the microorganisms themselves may regulate the power output simply and reliably. Then again, biocells may furnish enough power to keep an individual soldier or a small, isolated group of men in touch with friendly forces. For extended missions or in emergencies, conventional power sources may not be convenient to take along or may not be available. A biocell fed with native organic materials, human food, or human refuse might do the job instead. Eventually, we may know enough to teach the average soldier how to improvise his own biochemical fuel cell with a minimum of prepared gear, using mainly materials from his surroundings. In closed ecologic systems, particularly in space, the biocell may perform the dual function of waste disposal and auxiliary power source.

Assuming successful development of biochemical fuel cells, we can foresee possible uses for them by people who are far from conventional power sources – explorers, archaeologists, geologists, naturalists, boating and camping enthusiasts. This would constitute a rather limited market, and production costs would have to be quite low to make it attractive. Other specialty uses and products competitive with higher-cost electric power may well become obvious as research proceeds. At present, however, I think the potentials for space, the military, and for fuel-poor underdeveloped areas are the only ones that justify more than a basic research effort.

It is precisely the exaggerated claims for, and distorted perspectives on, the potential usefulness of the biocell that have retarded acceptance of this concept by responsible administrators of R&D. We must recognize the limitations of the device as they appear today but at the same time not underestimate its true potentials. Furthermore, some useful serendipic knowledge is bound to evolve from any interdisciplinary bio-electrochemical-catalytic efforts.

Conclusion

Thus far, we have many promises but few facts on which to base valid perspectives on biochemical fuel cells. [I hope that today's papers will provide us not only with solid facts but, equally important, with stimulating ideas for a variety of worthwhile efforts in this scientifically fascinating and technologically promising area.]

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